

# A Polarographic Investigation of the Kinetics of Epoxidation of Unsaturated Fatty Acid Esters<sup>1</sup>

CONSTANTINE RICCIUTI, LEONARD S. SILBERT,<sup>2</sup> and WILLIAM S. PORT,  
Eastern Regional Research Laboratory, Philadelphia, Pennsylvania<sup>3</sup>

IN A PREVIOUS PAPER (3) we reported that the second order specific reaction constants for the perbenzoic acid epoxidation of vinyl oleate and vinyl laurate at 30°C. were, respectively,  $1580 \times 10^{-3}$  and  $7.13 \times 10^{-3}$  l./mole/min. The specific reaction rate constants for the corresponding reactions with peracetic acid would be of greater interest because of the commercial use of peracetic acid for epoxidation. However this kinetic study was precluded by the interference of hydrogen peroxide and diacetyl peroxide in the analysis of commercial peracetic acid. Since our earlier work however the homologous long-chain aliphatic peracids have been synthesized in pure form (2). Specific reaction rate constants obtained, using such an acid, would be expected to be closely related to those from peracetic acid. Furthermore a non-aqueous polarographic technique has been devised (2) which specifically measures peracid content, making valid kinetic data taken even at high conversions. A redetermination of our previously reported results, using perlauric acid, was therefore desirable.

## Experimental

### APPARATUS

A Sargent<sup>4</sup> Model XXI polarograph was used to obtain the current-voltage curves. The capillary had  $m$  and  $t$  values of 3.13 mg. per second and 1.5 seconds, respectively, yielding a capillary constant of  $2.29 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$ . These values were obtained by using an open circuit with the capillary dipping into the electrolytic solution maintained at  $25 \pm 0.1^\circ\text{C}$ . The electrolytic solution consisted of 0.25  $M$  ammonium acetate in glacial acetic acid. The polarographic behavior of perlauric acid has been described in a previous publication (2).

### MATERIALS USED

*Perlauric acid* was prepared by the method of Parker (2) from distilled lauric acid, m.p. 43–44°C.

*Methyl laurate*,  $n_D^{20}$  1.4275, sap. no. 214.5 (theory 214.3), was prepared by the acid-catalyzed esterification of lauric acid with methanol, followed by fractional distillation of the crude methyl laurate.

*Vinyl laurate* and *vinyl oleate* were prepared by the procedure of Swern and Jordan (4).

*Methyl oleate* was prepared by the procedure of Knight (1).

*Ethyl epoxystearate* was prepared by the peracetic acid epoxidation of ethyl oleate and was crystallized from methanol. It had an oxirane oxygen content of 4.93 (theory 4.91),  $n_D^{20}$  1.4460.

### ANALYTICAL PROCEDURE

The epoxidation reactions were performed by mixing benzene solutions of weighed quantities of perlauric acid and the fatty acid ester and diluting with benzene so that the final concentrations were about 0.1 molar for each reactant. The solution was immediately transferred to the reaction cell maintained at the temperature of the investigation (15°, 25°, or  $35^\circ \pm 0.1^\circ\text{C}$ ). Two-ml. samples were pipetted from the mixture and transferred to the polarographic H-cell containing 50 ml. of the glacial acetic acid-ammonium acetate electrolytic solution. The H-cell was then sealed and degassed for 10 min. with nitrogen to remove dissolved oxygen. At the end of this period a polarogram was recorded. It was found that, because of the extreme dilution of the sample in the H-cell ( $10^{-4}M$ ), there was negligible reaction between the peracid and the unsaturated fatty acid ester during the time required for degassing and recording the polarograms.

Because the polarographic waves of the peracids yield abnormally high maxima, it was necessary to work at low concentrations. Sample sizes were chosen so that the final concentration of the peracid in the H-cell was about  $4 \times 10^{-3}M$ . At these low concentrations the maxima were sufficiently suppressed for reproducible wave heights to be obtained, provided the wave heights were measured in the flat portion of the curves (applied voltage range  $-0.9$  to  $-1.5$  volts). Samples were withdrawn at intervals and polarographed as described above. Diffusion currents were calculated from the perlauric acid wave heights, after correction for residual current.

The principal reactions studied were the rate of disappearance of perlauric acid in the presence of vinyl oleate, methyl oleate, and vinyl laurate at 15, 25, and  $35^\circ\text{C}$ . In addition, there were investigated the rates of induced decomposition of perlauric acid by the solvent, by methyl laurate (selected as a saturated ester of the parent acid), and by the reaction product (for which ethyl epoxystearate was selected as typical).

## Results and Discussion

No diminution of the polarographic wave heights of perlauric acid by either the solvent, methyl laurate, or ethyl epoxystearate was observed in the reaction period of the experiment and in the temperature range of interest. Therefore it was concluded that induced decomposition would not occur in the reactions studied and that changes in the measured concentration of perlauric acid would be caused solely by the reaction of perlauric acid and an olefin.

In Table I are listed the diffusion currents calculated from the observed wave heights for residual perlauric acid at the time and temperature given for the reactions of perlauric acid and methyl oleate, vinyl oleate, and vinyl laurate. The second order

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<sup>2</sup> Senior Fellow, National Renderers Association. Presently member of staff, Eastern Regional Research Laboratory.

<sup>3</sup> A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

<sup>4</sup> Mention of a specific trade name does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.

TABLE I  
Kinetics Data for the Epoxidation of Unsaturated Fatty Acid Esters with Perlauric Acid in Benzene

Methyl oleate			Vinyl oleate			Vinyl laurate	
15°C. 0.0969 <i>M</i> <sup>a</sup> 0.0978 <i>M</i> <sup>b</sup> 0.122 ± 0.014 <sup>c</sup>			15 0.0936 0.1073 0.145 ± 0.010			25 0.1008 0.0979 0.012 ± 0.003	
25 0.0928 0.0997 0.232 ± 0.017			25 0.0957 0.0978 0.270 ± 0.012			35 0.0952 0.1007 0.476 ± 0.034	
35 0.0984 0.1133 0.465 ± 0.036							
<i>t</i> (min.)	<i>i</i> (μa)	<i>t</i>	<i>i</i>	<i>t</i>	<i>i</i>	<i>t</i>	<i>i</i>
0	26.0	0	24.0	0	35.6	0	36.2
7	24.7	3	21.4	7	30.6	2	32.7
20	21.6	12	19.4	23	25.9	29	15.9
38	18.8	38	14.7	65	18.6	57	11.7
55	16.0	46	10.9	82	16.3	64	11.7
73	13.0	84	8.60	101	14.6	83	7.81
92	13.5	106	6.80	121	12.8	101	6.40
102	12.1	130	5.64	145	11.4	119	5.42
158	8.68	161	4.60	212	8.60	144	4.50
181	8.40	180	4.20	251	7.40	184	3.22
201	7.84	200	3.40				
261	5.40	246	2.88				
282	5.38	290	2.18				

<sup>a</sup> Perlauric acid; <sup>b</sup> fatty acid ester; <sup>c</sup> *k* (l. mole<sup>-1</sup> min.<sup>-1</sup>)

specific rate constant, *k*, was calculated from the equations:

$$k = \frac{1}{t} \left( \frac{1}{d-x} - \frac{1}{d} \right)$$

$$x = \frac{i_t}{i_0} \cdot d$$

where *t* = time in minutes, *d* is the mean of the initial concentration of the perlauric acid and the fatty acid ester in moles per liter, *x* is the residual concentration of the perlauric acid at time *t*, *i<sub>t</sub>* is the diffusion current at time *t*, and *i<sub>0</sub>* is the diffusion current at the start of the reaction (*t* = 0). The epoxidation of vinyl laurate was studied at only one temperature because the rate of reaction was so low that the experimental error (about 25%) would make meaningless any calculations of activation energy. If the measured value for the specific reaction rate constants at 25°C. for vinyl laurate (0.012 ± 0.003) and for methyl oleate (0.232) are compared, it may be concluded that the rate of epoxidation by an aliphatic peracid of an internal double bond is 15–26 times that of a vinyl double bond.

Activation energies and frequency factors for the perlauric acid epoxidation of methyl oleate and of vinyl oleate were found from the product of the gas constant *R* and the slope of the lines obtained by plotting  $-\ln k$  against  $\frac{1}{T}$  (Figure 1) and from cal-

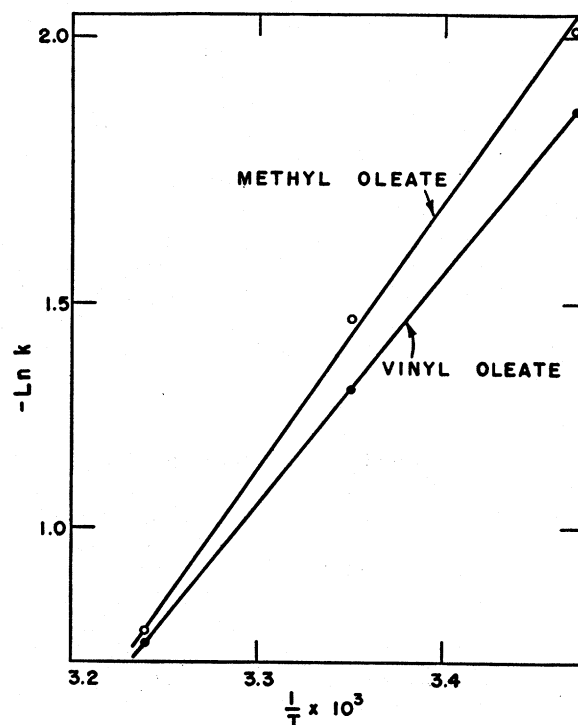


Fig. 1. Arrhenius plot for the reaction of methyl oleate and vinyl oleate with perlauric acid.

culations using the Arrhenius equation. For the perlauric acid epoxidation of methyl oleate  $E = 11.5$ ,  $A = 5.53 \times 10^7$ ; and for vinyl oleate  $E = 10.3$  K cal./mole,  $A = 8.61 \times 10^6$  l./mole/min.

From Figure 1 a value of  $350 \times 10^{-3}$  l./mole/min. at 30° may be interpolated for the specific reaction rate constant for the reaction of vinyl oleate and perlauric acid. If this value is compared with the previously reported value of  $1580 \times 10^{-3}$  for the reaction of perbenzoic acid and vinyl oleate at 30°, it may be concluded that the epoxidation by an aromatic peracid proceeds at about 4.5 times the rate by an aliphatic peracid.

### Summary

A polarographic technique which uses a non-aqueous electrolytic solution consisting of 0.25 *M* ammonium acetate in glacial acetic acid is a suitable medium for the investigation of the kinetics of fatty acid ester epoxidations. From the polarographic

data the specific reaction rate constants for the perlauric acid epoxidation of vinyl laurate, methyl oleate, and vinyl oleate in benzene at 25°C. were found to be 12, 232, and  $270 \times 10^{-3}$  l./mole<sup>-1</sup> min.<sup>-1</sup>. The Arrhenius equation for the epoxidations of methyl oleate and vinyl oleate by perlauric acid can

$$\text{be expressed as } k = 5.53 \times 10^7 e^{\frac{-11,500}{RT}} \text{ and } k = 8.61 \times 10^6 e^{\frac{-10,300}{RT}}.$$

### REFERENCES

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